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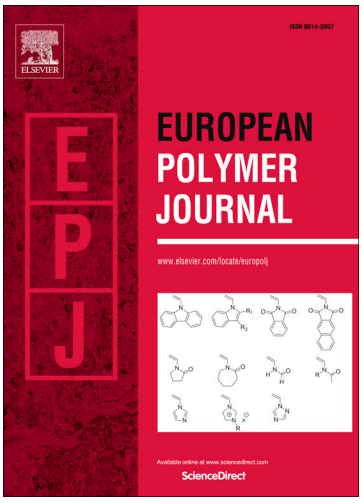

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Facile Synthesis of Reversibly Crosslinked Poly(ionic liquid)-type Gels: Recyclable Supports for Organocatalysis by *N*-Heterocyclic Carbenes

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ABSTRACT:

Owing to their broad modularity, polymeric versions of ionic liquids, referred to as poly(ionic liquids) (PILs), have attracted increasing attention as recyclable polymer-supported (pre)catalysts for various chemical transformations. Herein, an imidazolium-based statistical copolymer based on PIL (= coPIL) is specifically designed by free-radical copolymerization of styrene and 4-vinylbenzylethyl(benz)imidazolium chloride. A selective ion-exchange reaction can be subsequently achieved to incorporate bio-sourced difunctional sebacate-type counter-anions, causing the physical crosslinking of the coPIL precursor via electrostatic interactions between pendant imidazolium moieties and sebacate dianions. The as-obtained gel-type precursor exhibits a thermally latent behavior in THF, proving advantageous for a facile manipulation and practical use for organocatalysis. Upon heating, typically at 80 ºC, interaction between the sebacate dianion and the proton in C2-position of the imidazolium moieties generates polymer-supported *N*-heterocyclic carbene units that act as catalytic active species towards NHC-organocatalyzed reactions, namely, benzoin condensation, transesterification and cyanosilylation. The PIL-based gel precursors can be restored, recycled and reused by simply cooling down, *i.e.* with no need of an external chemical reagent, due to the shift of the intramolecular equilibrium towards the formation of imidazolium sebacate-type units. Overall, this novel gel-type copolymeric platform shows a thermo-responsive behaviour, and proves particularly versatile for heterogeneous organocatalysis.

KEYWORDS: *N*-Heterocyclic carbene, organocatalysis, poly(ionic liquid), masked-carbene

INTRODUCTION:

Polymeric versions of molecular ionic liquids (ILs), namely, poly(ionic liquid)s or polymerized ionic liquids, abbreviated as PILs, have attracted a great deal of attention as a new class of polyelectrolytes in the past two decades.[1–5] In PILs, cationically or anionically charged monomer units are covalently tethered to the polymer backbone, while counter-ions generally show high mobility. Typical organic cations of PILs include imidazolium, pyridinium and phosphonium groups, which can be associated to anions, such as Cl^-, Br^-, BF_4^-, $CH_3SO_3^-$, $(CF_3SO_2)_2N^-$, $CH_3CO_2^-$, etc.[6,7] A very broad range of PILs with a large number of functionalities have been designed, either following a chain-growth or a step-growth polymerization pathway, sometimes involving a post-chemical modification step of a polymer precursor.[3] Subsequent exchange of the counter-ion, referred to as ion metathesis, provides another means to tune PIL properties.[1] PILs thus combine essential features of ILs, including a high CO_2 solubility and a high ionic conductivity, with inherent qualities of polymers. These combined properties make PILs highly attractive in various applications, for instance, in analytical chemistry,[8] gas separation,[9] precursors of porous structures and nanostructured carbon-based materials,[10] as solid ionic conductors for energy storage,[11] and for catalysis as well,[3,12] which is the topic of the present contribution.

In the latter case, PILs eventually play two distinct roles. On the one hand, they can serve as efficient polymeric stabilizers of metal nanoparticles (NP), forming PILs@NP nanohybrids [13] in which the presence of PIL chains allows minimization of metal coalescence, providing efficient electrostatic + steric (= electrosteric) stabilization.[14] On the other hand, PILs can also operate as versatile polymeric supports of various types of catalysts.[15,16] For the general purpose of organocatalysis, PILs featuring sulfonic acid or proline moieties can for instance be employed as polymer-supported Brønsted acids and Lewis bases, respectively.[3] Furthermore, imidazolium-based PILs are handy precursors of polymer-supported *N*-heterocyclic carbenes (= polyNHCs).[17–22] Such polyNHCs can either be employed for reference organocatalyzed reactions of molecular chemistry, or serve as polymer-supported ligands for transition metals, *i.e.* forming polyNHC-metal derivatives,[19] by analogy with molecular NHC counterparts.[23] The latter polymer-supported metallic complexes have been advantageously employed to catalyze various organometallic reactions. In many of these catalysis applications, "task specific PILs" have been found to greatly facilitate separation, recovery and reuse, *i.e.* recycling of the polymer-supported (pre)catalysts –most often by simple filtration– and/or to improve stabilization of PILs@NP nanohybrids.[13,24]

In this context, imidazolium-based PILs featuring anions such as hydrogen carbonate, HCO_3^-, [20] or acetate, CH_3COO^-,[21,22] have been shown to serve as efficient air-stable progenitors of polyNHCs. This relates to the weakly basic character of both counter-anions interacting with the proton in C2-position of pendant imidazolium rings. Specifically, the imidazolium acetate-containing PILs exhibit a thermally latent behavior when employed in organocatalyzed reactions, and their catalytic activity can be turned on and off by a simple temperature increase and decrease.[21,25] Furthermore, such precursors can be readily recycled and reused, with no need of an exogenous chemical reagent, owing to the aforementioned intramolecular and temperature-dependent interaction between the acetate and the imidazolium moiety.[21] This convenient way of masking and manipulating polymer-supported NHCs can be further exploited, as discussed in the present contribution. By incorporating a commercially available and bio-sourced dicarboxylic acid, namely, sebacic acid, imidazolium-based physically crosslinked PIL gels can be achieved, and be readily manipulated and recycled for various NHC-organocatalyzed reactions. Here we describe for the first time the design of gel-supported NHC precursors from imidazolium-based PILs that are physically crosslinked, *i.e.* the crosslinking process is reversible, through the formation of a bis-carboxylate-type reagent. In addition, such gel-supported NHC precursors exhibit a thermally latent behavior when used in selected organocatalyzed reactions, namely, benzoin condensation, transesterification and cyanosilylation, which enables the manipulation of the catalytic activity by a simple temperature change. Overall, this novel polymeric platform is proven to be particularly flexible for heterogeneous organocatalysis.

EXPERIMENTAL SECTION:

Instrumentation

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AVANCE I spectrometer in appropriate deuterated solvents. All ^{13}C NMR measurements were carried out at 298 K on a Bruker Avance III HD 400 spectrometer operating at 100.7 MHz and obtained over 6144 scan with a 30º flip angle (90º pulse = 9µs), an acquisition time of 1.3 s, a relaxation delay of 3 s and 65 k data points. All ^{19}F NMR measurements were carried out at 298 K on a Bruker Avance III HD 400 spectrometer at 470.4 MHz. All HSQC (heteronuclear single quantum correlation) measurements were also performed at 298 K on a Bruker Avance III HD 400 spectrometer operating at 400.33 MHz. THF soluble polymers were previously

modified inserting TFSI as counter-anion and their molar masses were determined by size exclusion chromatography (SEC) in THF in presence of 10mM LiTFSI as eluent (1 mL / min) at 40 ºC using both refractometric (RI) and UV detectors (Varian).[26] Analyses were performed using a three-column set of TSK gel TOSOH (G4000, G3000, G2000 with pore sizes 20, 75, 200 Å respectively, connected in series). A Bruker spectrometer was used for ATR-FTIR analysis. Differential scanning calorimetry (DSC) measurements were carried out with a Q1000 apparatus from TA Instruments. DSC experiments were performed with aluminum sealed pans. A constant heating/cooling rate of 10 ºC/min and gas purging (N_2) at a flow rate of 100mL/min was used for all experiments. Thermogravimetric analyses (TGA) were performed using a TA instrument Q50 under a nitrogen atmosphere, from temperature (10 ºC / min) to 800 ºC. The weight loss was recorded as a function of temperature. The macroporous gel was examined using scanning electron microscopy (SEM) in a JEOL JSM-6360 microscope operating at an accelerating voltage of 20kV and 5000/10000 magnification.

Materials

Benzimidazole (≥95%), ethyl bromide (99%), 4-vinylbenzyl chloride (90%), lithium bis(trifluoromethane)sulfonylimide and Amberlite® IRA400 (hydroxide form) were obtained from Aldrich and cleaned by passing a mixture of water/methanol prior to use. Azobis(2-methylpropionitrile) (AIBN, 99%) was received from Aldrich and was recrystallized from methanol. Styrene and 4-vinylbenzylchloride (90%) were dried over CaH_2 and distilled prior to use. Sebacic acid (98%) and potassium hydroxide (KOH) were obtained from Alfa Aesar and benzimidazole (99%) was obtained from TCI and used as received. Tetrahydrofuran (THF) was distilled over Na/benzophenone. Ethyl acetate, acetonitrile and methanol (99.7%, Aldrich) were used without further purification. Pre-wetted dialysis tubing with a cut-off of 10 kDa (Spectra/Por® 6 Standard RC) was obtained from Spectrumlabs.

General Procedures

Synthesis of N-ethylbenzimidazole (1). Benzimidazole (8 g, 67.72 mmol) was dissolved in DMF (45 mL) and 7.6 g (135 mmol) of potassium hydroxide were added. The solution was stirred for 1 hour, and 5.5 mL (74.5 mmol) of ethyl bromide were added dropwise. After stirring at RT for 24 h, the solution was diluted in 100 mL of water and extracted with chloroform (3 x 25 mL). Organic phases were combined, dried over $MgSO_4$ and evaporated, yielding a yellow viscous oil (yield: 80%; 7.9 g). ^{1}H NMR (DMSO-d_6): δ =

8.25 (s, 1H, N-CH-N), 7.69-7.20 (m, 4H, aromatics), 4.12 (t, 2H, N-CH_2-CH_3), 1.32 (t, 3H, -CH_3). ^{13}C NMR (DMSO-d_6): δ = 144.5, 143.7, 123, 119.8, 110, 43.1, 14.8

Synthesis of 4-vinylbenzylethyl(benz)imidazolium chloride ([ViEBIm]Cl) by quaternization (2). 1-vinyl-4-chloromethylstyrene (8.37 mL, 59.4 mmol) and 7.9 g (54 mmol) of **1** were dissolved in acetonitrile (20 mL) and heated to 80 ºC for 24 h. The solvent was evaporated and the resulting powder was washed with diethyl ether. The product was dried for 8h under vacuum, yielding a white powder (yield 77%, 12.41 g). ^{1}H NMR (DMSO-d_6): δ=9.68 (s, 1H, N-CH-N), 8.12-7.14 (m, 8H, aromatics), 6.72 (dd, 1H, Ph-CH-CH_2), 5.95 (s, 2H, Ph-CH_2-N), 5.76 (d, 1H, CH=CH_2), 5.25 (d, 1H, CH=CH_2), 4.15 (dd, 2H, N-CH_2-CH_3), 1.31 (t, 3H, -CH_2-CH_3). ^{13}C NMR (DMSO-d_6): δ = 142, 136.2, 135, 133.8, 131.5, 128.8, 128.7, 126.5, 126.3, 114.1, 113.5, 58.6, 44.5, 14.9

Synthesis of polystyrene-co-poly(4-vinylbenzylethyl-(benz)imidazolium chloride) (PS-co-Poly[ViEBIm]Cl) (3) by free-radical copolymerization. 5 g (0.167 mmol) of **2**, 3.84 mL (0.335 mmol) of styrene, 41 mg of AIBN and 20 mL of dry methanol were added in a Schlenk tube. Five freeze-thaw pump cycles were performed and the solution was stirred at 75 ºC for 12h. The resulting compound was purified by two dialyses against methanol (10kDa MWCO). (Yield: 38%; final composition: 63% styrene / 37% of **2**). ^{1}H NMR (DMSO-d_6): δ=10.5 (br, 1H, N-CH-N), 8.22-5.68 (br, 16.5, aromatics), 5.9-5.5 (br, 2H, Ph-CH_2-N), 4.6-4.4 (br, 2H, -CH_2-CH_3), 2.1-0.9 (br, 12.7H, CH-CH_2 backbone, CH_3 ethyl chain); see Fig. S1.1, S1.7, S2.1, S3.1, S4.1, S4.4).

Synthesis of Polystyrene-co-poly(4-vinylbenzylethyl-(benz)imidazolium sebacate) (PS-co-Poly[ViEBIm]Seb)(5) by anion metathesis using Amberlite resin. 4 g of Amberlite® IRA 400 OH^- were taken in a round bottom flask and agitated for 12 h in a 50:50 MeOH : H_2O solution. Finally, the resin was filtered and air-dried. The resin was suspended in 15 mL of MeOH and 1g of polymer **3** was added to the solution and stirred for 10 minutes. Sequential addition of 0.215 g (0.106 mmol) of sebacic acid were added to the solution and stirred for 15 minutes. Note that addition in sequence was preferred owing to the instability known to OH^- anions in imidazolium derivatives that can lead to hydrolysis.[27–29] The solution was filtered and dried under vacuum to yield a yellowish powder (yield 94%). ^{1}H NMR (DMSO-d_6): δ=11.4 (br, 1H, N-CH-N), 8.22-5.68 (br, 16.5, aromatics), 6-5.5 (br, 2H, Ph-CH_2-N), 4.6-4.4 (br, 2H, -CH2-CH_3), 2.2-0.9 (br, 12.7H, CH-CH_2 backbone, CH_3 ethyl chain, CH_2-CH_2 sebacate, CH_2-CH_3 sebacate); see Fig. S1.2, S1.8, S2.1, S3.2, S4.2, S4.4.

Synthesis of gel-supported pre-catalysts. 0.251 g of **5** were dried by azeotropic distillation in dry THF (3x5 mL) in a Schlenk tube. After, polymer **5** powder was suspended in THF (0.5 M) and heated at 80 ºC for 4 hours, yielding a physically-crosslinked insoluble orange gel (yield 99%).

Synthesis of PS- co -poly(4-vinylbenzyl-NHC-CS_2) (6). In a Schlenk tube, 41 mg of gelled **5** were suspended in 5 mL of dry MeOH. CS_2 (0.5 mL; 8.3mmol) was then added and the mixture was stirred at 80 ºC for 48h when the formed **6** became soluble in the solvent (MeOH) dissolving the gel. The solvent and the excess of CS_2 were evaporated, forming a reddish powder (PS-*co*-Poly[ViEBIm]CS_2); (see Fig. S1.9): ^{1}H NMR (DMSO-d_6): δ= 12.3-11.8 (br, 1H, -COOH) 8.22-5.98 (br, 16.5, aromatics), 6-5.5 (br, 2H, Ph-CH_2-N), 4.6-4.4 (br, 2H, -CH2-CH_3), 3-0.8 (br, 12.7H, CH-CH_2 backbone, CH_3 ethyl chain, CH_2-CH_2 sebacic acid, CH_2-CH_3 sebacic acid) [21]

Benzoin Condensation. In a typical experiment, 0.251 g (0.446 mmol) of gelled **5** and a portion of 4 mL of THF were added and 0.455 mL (4.46 mmol) of benzaldehyde was added in a Schlenk tube. The reaction mixture was stirred for 24 h at 80 ºC. The mixture was allowed to cool down to room temperature, and the liquid phase removed and analyzed. This phase was analysed by ^{1}H NMR in DMSO-d_6. Benzoin conversion was determined by ^{1}H NMR in DMSO-d_6 by comparing the integral value of the aldehyde signal of benzaldehyde (d, 10ppm) with the one of the –CH- benzoin signal (d, 6 ppm) (Fig. S1.13). The swollen gel was dried and cleaned with dry THF at 40 ºC twice. Finally, the same quantity of dry THF was added enabling the next run of catalysis. Note that every cycle the polymer-supported catalyst was weight and no loss of catalyst was observed.

Transesterification. In a typical experiment, 0.170 g (0.3 mmol) of **5** were previously gelled and a portion of 4 mL of THF was added. Then 0.32 mL (3 mmol) of benzyl alcohol and 0.30 mL (3.27 mmol) vinyl acetate were added. The mixture was stirred for 2 h at 80 ºC. After cooling down to room temperature, the liquid phase was retired and analyzed by ^{1}H NMR in DMSO-d_6 and conversion calculated comparing the integral value of the –CH_2- benzyl alcohol signal (4.5 ppm) to that of the –CH_2- benzyl acetate signal (d, 5ppm) (Fig. S1.14). The swollen gel was dried and cleaned with dry THF at 40 ºC two times. Finally, the same quantity of dry THF was added to perform next catalytic run using the same catalyst.

Cyanosilylation. In a typical experiment, **5** (0.1 g; 0.176 mmol) was previously gelled in THF as explained in Fig. 2. A portion of 4mL THF was then introduced, and then 0.18 mL

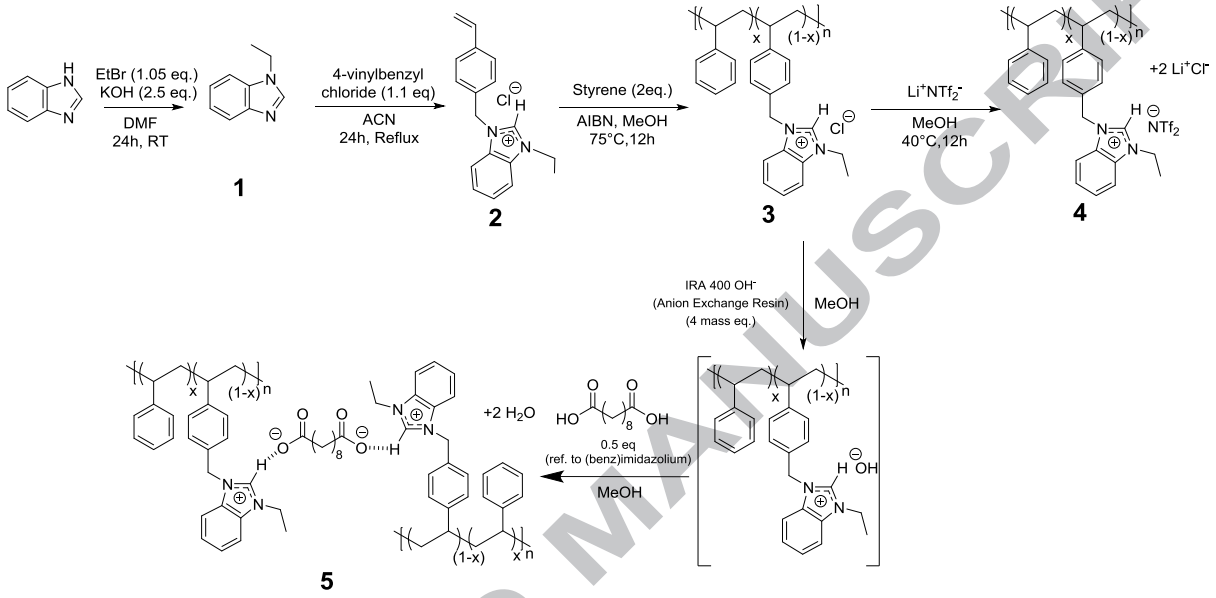
(1.76 mmol) of benzaldehyde and 0.24 mL (1.9 mmol) trimethylsilyl cyanide (TMSCN) were added. The mixture was stirred for 1 h at 80 ºC. After cooling down to room temperature, the liquid phase was removed and analyzed by ^{1}H NMR in DMSO-d_6 and conversion of α-trimethylsilyloxy-phenylacetronitrile calculated comparing the integral value of aldehyde signal (10 ppm) to that of the –CH- cyanide product (d, 5.5 ppm). The swollen gel was dried and cleaned with dry THF at 40 ºC twice. The same amount of dry THF was added to proceed to the next catalytic run (see Fig. S1.15).

Procedure for reversibility of gels. 0.1g (0.176mmol) of **5** previously gelled in THF was dried under vacuum. Gel **5** was suspended in methanol afterwards and heated at 40 ºC. Then, 0.505 g (1.76 mmol) of LiTFSI were added and let stir overnight. The polymer (PS-*co*-poly[ViEBIm]TFSI)-2 (**7**) became insoluble after the anion metathesis. The excess of methanol and LiTFSI was removed and the precipitated polymer washed with water and (PS-*co*-poly[ViEBIm]TFSI)-2 (**7**) recovered (yield 71%) (Fig. S1.4, S1.6, S1.11). The same procedure was applied to (PS-*co*-poly[ViEBIm]Cl) (**3**) in order to obtain the (PS-*co*-poly[ViEBIm]TFSI)-1 (**4**) as well (yield 80%; see Fig. S1.3, S1.5, S1.10).

RESULTS & DISCUSSION:

3.1. Synthesis, characterization and manipulation of gel-supported pre-catalysts. A statistical copoly(ionic liquid) (coPIL), namely, polystyrene-*co*-poly(4-vinylbenzylethyl-(benz)imidazolium chloride), denoted as PS-*co*-Poly[ViEBIm]Cl (**3**), was prepared by free-radical copolymerization of 4-vinylbenzylethylbenzimidazolium chloride (**2**) and styrene, using AIBN as a radical source (Scheme 1). Benzimidazolium- rather than imidazolium-type units as reported in previous works [22] were introduced here, owing to their slightly higher proton-acidity in the C_2 position. It was thus expected that the equilibrium could be better shifted towards the formation of the NHC active species. After 12 h of reaction achieving 50% monomer conversion, the resulting copolymer was chemically modified into the coPIL **4** possessing non-coordinating anions, namely, bis(trifluoromethane)sulfonylimide (TFSI) = $(CF_3SO_2)_2N^-$, prior to characterization by size exclusion chromatography (SEC) in THF containing 10 mM LiTFSI. This was readily achieved by anion exchange, as previously reported.[26] The as-obtained TFSI-containing coPIL **4** exhibited a unimodal distribution of molar masses with a dispersity (*Đ*) of 1.35 (Fig S6.1). Copolymer **3** then served as precursor for the synthesis of a physically crosslinked gel *via* anion metathesis converting **3** into PS-*co*-

Poly[ViEBIm]Seb (**5**). The commercially available Amberlite® IRA-400 hydroxy resin was employed for this purpose, providing an entirely metal-free synthetic route to the imidazolium-based physically crosslinked gel (Scheme 1).[30] The anion exchange reaction indeed allowed substituting OH^- counter-anions for Cl^- ones and further introduction of sebacic acid yielded copolymer **5** and water as side product.[31]



Scheme 1. Synthetic route to (PS-*co*-Poly[ViEBIm]Cl) (**3**) by free radical copolymerizacion of [ViEBIm]Cl and styrene in methanol, followed by the synthesis of physically crosslinked (PS-*co*-Poly[ViEBIm]Seb) (**5**) by anion exchange. Synthesis of (PS-*co*-Poly[ViEBIm]TFSI)-1 (**4**) is also displayed.

In addition to being a non-fossil bio-based resource, sebacic acid contains two carboxylic acidic groups with a similar pKa ~4.6 to that of acetic acid, *i.e.* the conjugated acid of acetate counter-anion that has been found to efficiently generate polymer-supported NHCs from imidazolium acetate-containing PILs.[20-21] Interestingly, copolymer **5** could be solubilized in DMSO, facilitating its structural characterization by NMR spectroscopy, whereas it was not soluble at all in solvents such as THF or acetonitrile. Near quantitative anion exchange reaction (~95%) was achieved, as determined by ^{1}H NMR spectroscopy (Figs. 1 & S2.2). Importantly, the characteristic proton of the C2-position of benzimidazolium units appearing at δ = 10.5 ppm in **3** was shifted downfield to δ = 11.5 ppm, as a consequence of the insertion of *bis*-carboxylate anions, while the signal at δ = 12.1 ppm that resulted from the resonance of the carboxylic acidic protons of sebacic acid disappeared. This attested to the formation of

hydrogen bond-type interactions between C2-protons of the imidazolium moieties and the carboxylate anions.

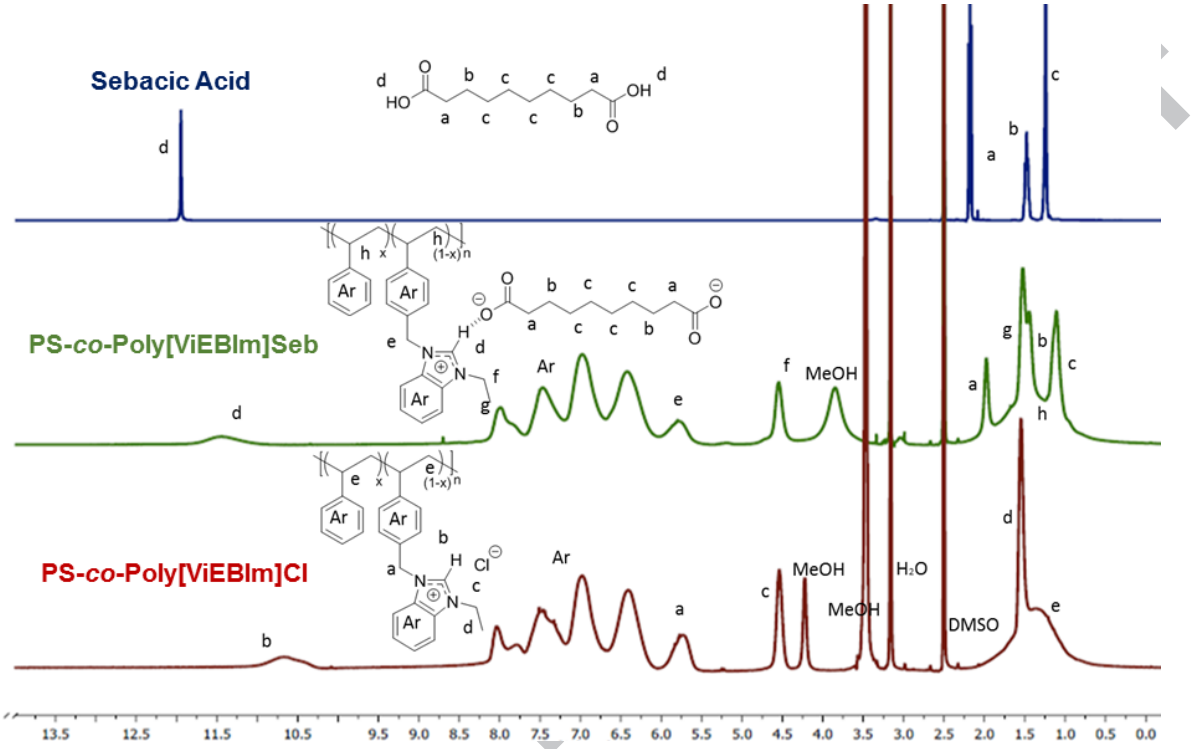


Figure 1. ^{1}H NMR (DMSO-d_6) showing the insertion of the sebacate forming the physical gel (PS-*co*-Poly[ViEBIm]Seb) (**5**) from (PS-*co*-Poly[ViEBIm]Cl) (**3**).

Characterization of the two copolymers by ^{13}C NMR spectroscopy (Fig. S1.7 and S1.8) confirmed the selective incorporation of sebacate anions, as evidenced by the presence of sebacate carboxylate single signal at δ = 177.7 ppm. This was also confirmed by FTIR spectroscopic analysis of copolymer **5**. The presence of a strong band at 1640 cm^{-1} (Fig. S.2.1) could be assigned to the C=O stretching of carboxylates. Thermogravimetric analysis also evidenced a significant change in the degradation profile, before and after anion exchange, the stability of the resulting imidazolium sebacate-containing coPIL **5** (Fig. S4.2) being lower than that of its parent copolymer **3** (5 wt. % loss observed at 200 and at 300 ºC, respectively; see Fig. S4.1, S4.4). This result was consistent with previous observations concerning imidazolium-type coPILs featuring acetate counter-anions.[21] This was also reflected in the T_g values, a T_g of 23 ºC being determined for the chloride-containing precursor **3** (Fig. S3.1), while coPIL **5** did not exhibit any clearly detectable T_g, likely due to its gel-like behavior.

Heating coPIL **5** at 80 ºC in THF for 4 h led to an orange swollen gel (see Fig. 2). This bathochromic effect could be due to an increase in electron donating ability from C2-benzimidazolium as a consequence of basic carboxylate insertion, leading to higher-energy associated HOMO as similarly found in some carbene metal ligands.[32] After drying, this physically crosslinked copolymer exhibited a porous monolith structure featuring open pores with pore sizes in the range 100 nm-10 µm, as revealed by scanning electron microscopy (SEM; Fig. 3). Such porosity was expected to enhance the interfacial mass and energy exchange and be beneficial for catalytic performance of the monolith. Unfortunately, this hypothesis could not be confirmed by analysis of the surface area by Brunauer–Emmett–Teller (BET), owing to the high heterogeneous porosity.[33]

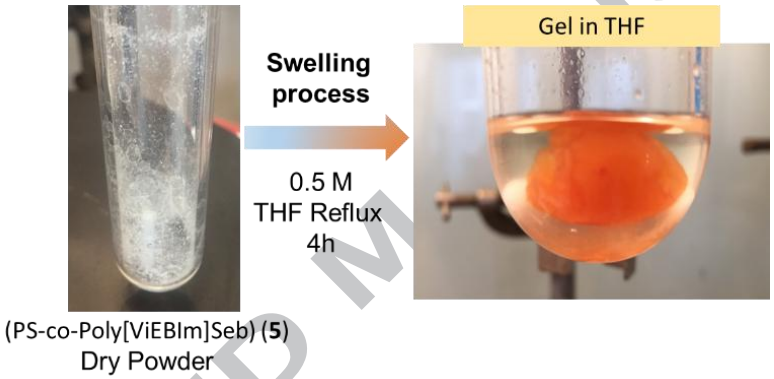


Figure 2. PS-*co*-Poly[ViEBIm]Seb (**5**) gelation procedure for heterogeneous supported catalyst synthesis in THF.

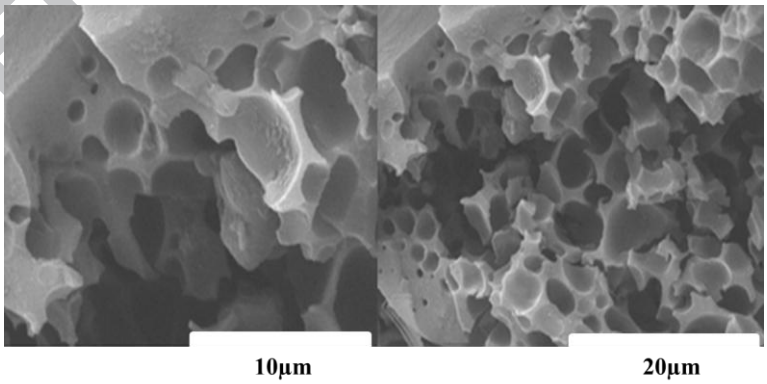
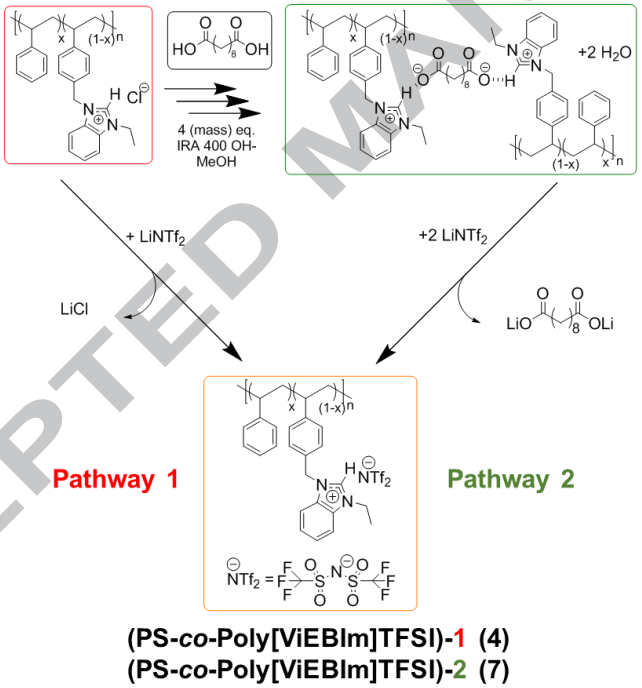


Figure 3. SEM pictures of polymer **5** as a heterogeneous catalyst support in organocatalysis showing pore sizes between 100 nm to 10 µm.

Owing to the absence of covalent bonds in the gel deriving from copolymer **5**, *i.e.* to the formation of physical crosslinking points, this gel could be easily manipulated by further

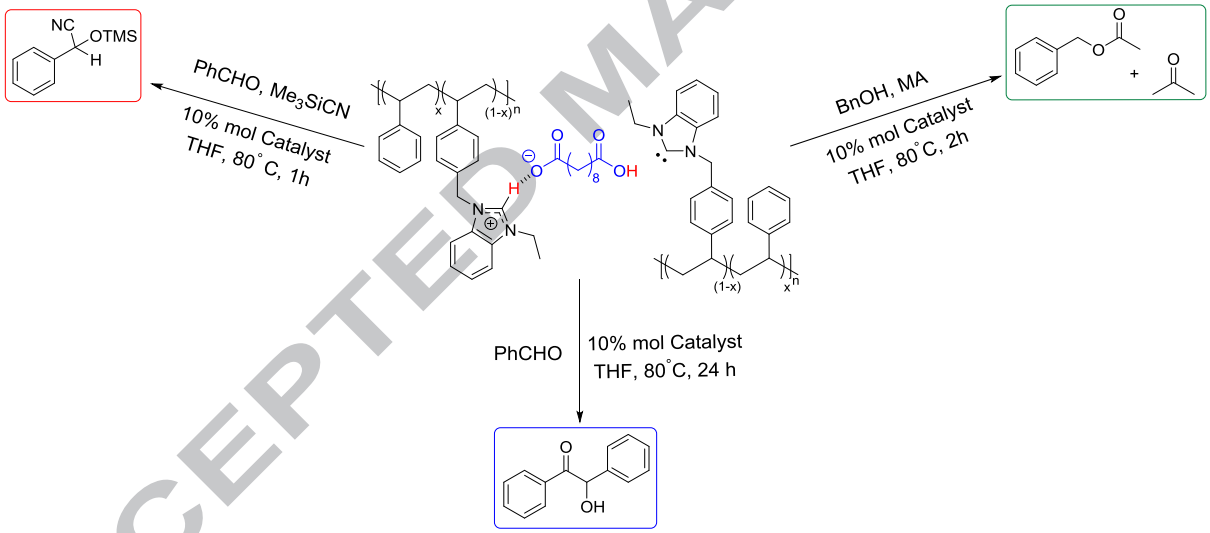
anion exchange, for instance, by using the non-coordinating TFSI anion.[3,4] In this way, the gel could be readily de-crosslinked, restoring a linear and eventually soluble copolymer (**7**; see Scheme 2). Addition of LiTFSI onto a methanol solution of gel **5** thus caused its gradual disruption, ultimately yielding a fully dissolved compound after 12 h of stirring. The corresponding ^{1}H NMR spectra of both TFSI-containing copolymers **4** and **7**, emanating from the same parent copolymer **3** proved to be identical (Fig. S1.12), validating the de-crosslinking method by anion exchange. This was also evidenced by analysis by ^{13}C and ^{19}F NMR spectroscopy of compounds obtained after anion exchange (see Fig. S1.5, S1.6, S1.10 and S1.11). In addition, SEC analysis of copolymers **4** and **7** showed chromatograms that were almost superimposable (Fig. S5.1). In other words, these results did not show any evidence of degradation or side reactions or aggregation phenomena occurring during the post-chemical modification of coPIL derivatives.



Scheme 2. Two different pathways followed for the synthesis of TFSI anion-containing copolymers (**4**, **7**) supporting the anion-exchange mediated decrosslinking of the gel.

3.2. Organocatalysis from gel-supported NHCs. The ability for coPIL-type gel **5** to *in situ* generate self-supported NHC units was first demonstrated by adding a large excess of CS_2 as electrophilic reagent.[21,34,35] This chemical post-modification step led to copolymer **6** consisting of polymer-supported NHC-CS_2 betaine-type adducts. The ^{13}C NMR spectrum of the as-obtained red solid compound showed the characteristic signal at δ = 231 ppm due to the

dithiolate group (CS_2^-; Fig. S1.9). Although this chemical transformation was not quantitative, as observed by signals corresponding to residual *bis*-carboxylate in ^{13}C NMR analysis, (Fig. S1.9), it provided an indirect proof for the *in situ* formation of polymer-supported NHCs. NHC-CS_2 adduct formation also allowed disrupting the physically crosslinked copolymer gel, leading to a copolymer-supported betaines soluble in methanol and corresponding free sebacic acid as by-product. Copolymer **5** was then employed as a gel-support of masked NHCs in three distinct benchmark NHC-organocatalyzed reactions, including benzoin condensation,[36] transesterification and cyanosilylation (Scheme 3). Of particular interest, NHC-type active species could be thermally activated with no need of an exogenous reagent, owing to the dynamic equilibrium between sebacate anions and protons of imidazolium units, enabling to switch the catalytic activity on and off upon heating and cooling, respectively. The temperature change also allowed us to easily recycle copolymer **5** and reuse if for subsequent catalytic cycles.



Scheme 3. Benzoin condensation, transesterification and cyanosilylation organocatalyzed by NHC-supported physically crosslinked porous gel under heterogeneous conditions.

Benzoin condensation was first implemented in THF using benzaldehyde as the substrate and 10 mol. % of copolymer **5** referred to imidazolium moieties. For sake of comparison, the TFSI- and chlorine-containing copolymers, **4** and **3**, were also tested under the same conditions. However, no benzoin product was obtained with the two latter precursors, corroborating the non-innocent role of carboxylate counter-anions to *in situ* generate catalytic polymer-supported NHCs. In contrast, conversions were in the range 65-70 % after 24 h in five consecutive catalytic cycles when gel **5** was applied (Fig. 4). As discussed, the benzoin

product was formed only upon heating at 80 ºC, *i.e.* no catalytic activity was noted at RT, presumably owing to the shift of the equilibrium to the formation of inactive imidazolium units. With the benzoin product being soluble in THF, the coPIL-type gel precursor **5** could be simply recovered by filtration due to its insoluble character. It could further be stored and handled in air for several weeks without apparent degradation. It could also be implemented both in the NHC-organocatalyzed transesterification and cyanosilylation reactions under heterogeneous conditions in THF (Scheme 3). The former reaction was performed using benzyl alcohol and vinyl acetate as substrates, which in presence of 10 mol % of **5** as gel-supported pre-catalyst, yielded benzyl acetate with conversions in the range 72-90% during 5 different catalytic cycles (Fig. 4). Finally, when treating benzaldehyde with trimethylsilyl cyanide (TMSCN) in presence of gel **5**, α-trimethylsilyloxy-phenylacetronitrile was obtained in near quantitative yields after 1h (Fig. 4). This series of results thus verified that **5** could be readily applied to a range of organocatalytic reactions and could be readily recycled, without any significant loss of catalytic activity (see Experimental for details). Overall, catalytic performances of coPIL gel **5** were found similar to those obtained with the different linear polymer-supported NHCs previously reported.[19,21,22,24]

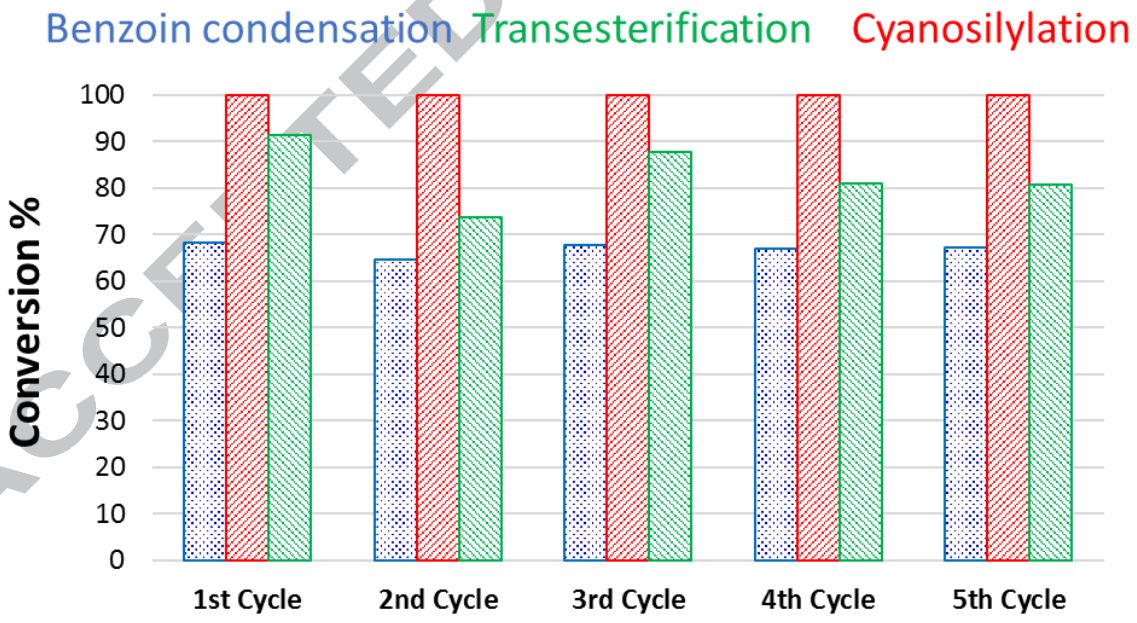


Figure 4. Different benzoin condensation, transesterification and cyanosililation average conversions obtained after 5 cycles using 10 mol % amount of catalyst for 24 h in THF under heterogeneous conditions

CONCLUSION:

Air-stable physically crosslinked porous gels swollen in THF were designed for the purpose of organocatalysis under heterogeneous conditions. This was achieved by free-radical copolymerization to obtain a statistical benzimidazolium-based styrenic-type copoly(ionic liquid), followed by a metal-free anion exchange reaction to incorporate dicarboxylate functions deriving from a biosourced dicarboxylic acid, namely, sebacic acid. Difunctional sebacate anions eventually played a dual role of i) ionic crosslinker and ii) slightly basic internal counter-anion to *in situ* deliver catalytically active NHC species upon heating. The as-obtained gels could be reversibly manipulated to regenerate a linear coPIL by anion exchange using a monofunctional anion. These distinctive advantages allowed performing standard molecular heterogeneous NHC-organocatalyzed reactions, leading to relatively high conversions in reaction products. The gel-like catalysts could be readily recycled up to 5 times, without any significant loss of catalytic activity or leaching. The catalytic performance could be tuned by thermal activation/deactivation, shifting the equilibrium either towards NHC active species, or to inactive imidazolium sebacate.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures, and related characterization data.

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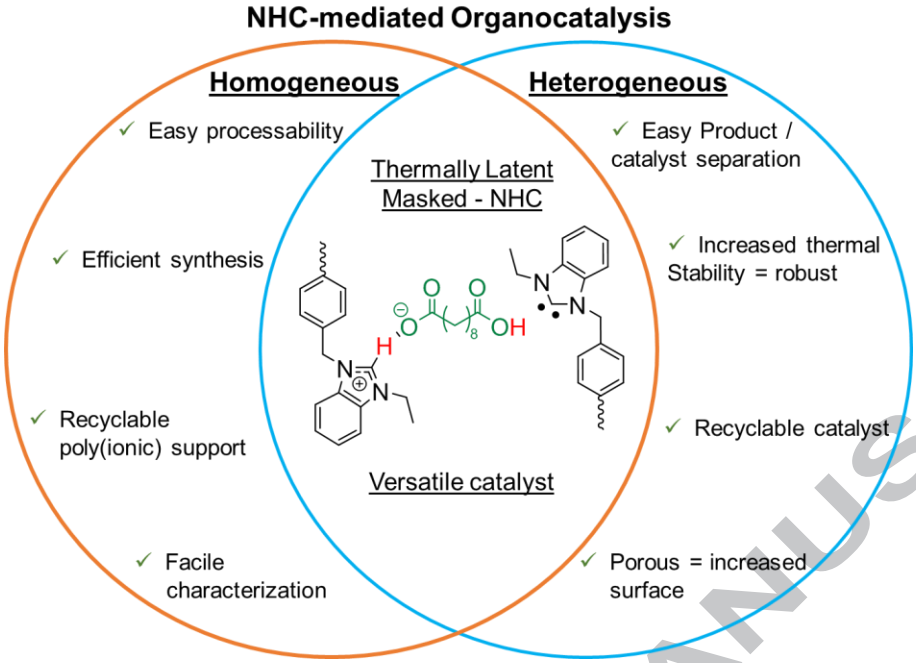
Graphical Abstract:



Highlights:

- A selective metal-free ion-exchange strategy is implemented to achieve physically crosslink imidazolium-based copoly(ionic liquid)s using sebacate as counter-anions.
- The gel-type structure serves as heterogeneous, easy-handling and thermally latent polymer-supported pre-catalysts based on *N*-heterocyclic carbenes (NHCs).
- Various NHC-organocatalyzed molecular reactions can be performed in presence of the physically crosslinked gel-supported pre-catalysts.
- The crosslinked gel can be recycled and reused without any loss of efficiency after 5 catalytic cycles.
- This work introduces an innovative alternative for supporting NHCs toward their facile manipulation for organocatalysis, exploiting the intrinsic reactivity of imidazolium-based copoly(ionic liquid)s.